SELECTIVE CATALYTIC REDUCTION OF NITROUS OXIDE WITH HYDROCARBONS USING A SO₂ RESISTANT Fe/ZEOLITE CATALYST

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Abstract

Removal of nitrous oxide (N₂O) from exhausts of chemical plants and certain combustion facilities is an effective way for substantial reduction of greenhouse gas emissions from anthropogenic sources. ECN has developed a catalyst for catalytic removal of N₂O from various exhaust gases using hydrocarbons (propane or methane) as reducing agent. The catalyst is an ion-exchanged zeolite, specially modified to improve its resistance against sulphur. In bench-scale tests, the catalyst has proven to perform at relatively low temperatures. In a synthetic flue gas containing oxygen and water, 90% conversion of N₂O to N₂ was reached at 350°C. Activity decreases slightly when NO and SO₂ are present. The catalyst was found to be resistant against all regular constituents of flue gases: O₂, H₂O, CO₂, CO, NO_x and most importantly SO₂. In stability tests, no apparent loss of activity was recorded in 2000 hours time-on-stream. The catalyst was originally developed for selective catalytic reduction (SCR) of N₂O, but recently it has also demonstrated strong activity in SCR of NO_x. The capacity to remove both NO_x and N₂O from the same gas mixture is an interesting development, since nearly all sources of N₂O also emit NO_x. Investigations are still going on, but the first results indicate that ECN's SCR catalyst has a great potential for integrated SCR of NO_x and N₂O with hydrocarbons from a variety of off-gases.

Key words

Nitrous oxide, selective catalytic reduction, hydrocarbons, zeolite, deNO_x, deN₂O.

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1. INTRODUCTION

In the industrialised world, elimination of nitrous oxide emissions can be regarded as one of the most viable methods for reduction of greenhouse gases. ECN's "Optiedocument" lists 61 options for reduction of greenhouse gas emissions. Nitrous oxide from nitric acid manufacture has the best potential (8.5 Mton) and one of the lowest costs. Since these emissions come from only a handful of plants, it is also one of the easiest accomplished. In the principal reaction N_2O oxidises a hydrocarbon. Oxygen is present to complete this oxidation:

All kinds of hydrocarbons can be used as reducing agent. Inexpensive options are methane (natural gas) or propane (LPG). In the case of nitric acid plants, hydrocarbons must be added. In other cases, especially if N_2O needs to be removed from a flue gas, enough hydrocarbons are already present in the exhaust, and no addition of a reducing agent is required. Normal sources emitting N_2O also emit NO_x . The catalyst developed by ECN for N_2O reduction also has the potential to remove NO_x using the same principle of Selective Catalytic Reduction (SCR) with the same hydrocarbons. The process is a competitor for regular de NO_x SCR using ammonia or urea, but it has clear advantages. Not only is the reducing agent cheaper and commonly available, also the risk of enhanced N_2O formation as a by-product of NO reduction is precluded. After all, the catalyst is designed to be an effective N_2O reduction catalyst.

2. EXPERIMENTAL

Catalysts have been prepared by simple ion-exchange of zeolites. Catalyst powder was compressed, crushed and sieved. Sieve fractions were subjected to activity tests in fixed-bed laboratory flow reactors. Stability tests were performed using ceramic monoliths (honeycombs) with the catalyst powder deposited on a washcoat. In activity tests, the gas mixtures were used simulating the exhausts of industrial plants. Standard conditions are a flow of 5 litre/min (STP) with 500 – 1500 ppm N_2O , 500 – 1500 ppm C_3H_8 , 6% O_2 , 2% H_2O , 5% CO_2 , balance N_2 . In some cases, (part of) N_2O was replaced by NO . The bed size was approximately 23 ml, resulting in a space velocity (GHSV) of $13,000 \text{ h}^{-1}$. All tests presented in this paper were performed at atmospheric pressure. Project partners performed the stability tests under slightly different conditions. The most important difference was the addition of 100 – 200 ppm SO_2 to verify stability in sulphurous off-gases.

3. RESULTS AND DISCUSSION

3.1 N₂O Removal with Fe/zeolite

The Fe/zeolite catalyst was subjected to standard activity tests with various gas mixtures. The results of these tests are presented in Figure 1. The most important observation was that addition of propane to a gas mixture enhanced the activity of the Fe/zeolite catalyst dramatically. It is represented by a shift in temperature. When comparing the curves of tests with N₂O + O₂ (×) with N₂O + O₂ + C₃H₈ (●), the same level of N₂O conversion is found at almost 200 °C lower temperatures when propane is added.

In real off-gases water is always present. Therefore, all other tests were performed in the presence of water. The presence of water has a negative effect on the performance of the catalyst. The activity curves shift about 50 °C upwards. Nevertheless, with water present, addition of propane results in the same dramatic increase of activity: a shift of about 200 °C between N₂O + O₂ + H₂O (outside graph, above 500 °C) and N₂O + O₂ + H₂O + C₃H₈ (◆). This substantially large enhancement of activity is characteristic for Fe/zeolite catalyst. Other catalysts also showed enhanced activity when adding propane, but the shift was smaller or even negligible.

Addition of CO₂, a common constituent of off-gases, did not influence the performance of the catalyst. Also, replacing half of N₂O with NO, did not alter the conversion of N₂O significantly. Tests with the Fe/zeolite catalyst in simulated flue gases containing SO₂ showed that activity decreases slightly, but that the catalyst is stable and active over a 2000 hour period. Based on these results, ECN has filed a patent application for the catalyst and the method of N₂O removal.

3.2 N₂O Removal with Modified Fe/zeolite

In the tests with ECN's first generation Fe/zeolite catalysts, incomplete propane combustion and emission of CO was noticed at temperatures where complete N₂O conversion was already reached. To avoid CO emission and hydrocarbon slip the operational temperature must be set higher than necessary for complete N₂O removal. This jeopardises the applicability of the catalyst. Emission of 1000 ppm CO and emission of unconverted hydrocarbons is undesirable. In particular the slip of methane, a greenhouse gas itself, cannot be justified as a side-effect of N₂O removal. Hydrocarbon slip and CO emission were simultaneously remedied by modification of the catalyst to enhance its oxidation performance. The difference between both catalysts is evident from Figure 2. The propane conversion neatly goes to completion in the same temperature range as N₂O. As a bonus N₂O conversion is improved as well. CO emission is eliminated except for a few dozen ppms, but this occurs at temperatures outside the normal operational range.

Therefore, it can be stated that ECN's modified Fe/zeolite catalyst is active and clean in the Selective Catalytic Reduction (SCR) of N₂O using hydrocarbons (e.g., propane) in the presence of H₂O, O₂, CO₂, NO and SO₂, without hydrocarbon slip or CO emission due to incomplete combustion.

3.3 Combination with NO removal

Since NO_x is found in nearly all exhausts that are eligible for N₂O abatement, the Fe/zeolite was tested in Selective Catalytic Reduction of NO_x using the same hydrocarbons. The catalyst is active, but not spectacular. The performance is comparable to similar catalytic system currently presented in the scientific literature. However, other ion-exchanged zeolites using different transition metals were successfully tested with conversion over 90% at temperatures identical to the temperature range where ECN's (modified) Fe/zeolite converts over 90% of N₂O. The idea is to use this coincidence and combine both catalysts in a single reactor. It would then become possible to integrate NO_x and N₂O removal using a single addition of hydrocarbons or the hydrocarbons already present in the off-gas.

Preliminary tests demonstrated that at 400 °C, conversion of NO_x, N₂O and propane exceeds 90% (250 ppm NO, 250 ppm N₂O, 1000 ppm C₃H₈, in the presence of O₂, CO₂ and H₂O). It shows that there is a great potential to reach the aim of integrated deNO_x/deN₂O with SCR using hydrocarbons.

4. FUTURE

The catalyst and catalytic system developed by ECN should first be applied to the exhaust of nitric acid plants. At the time of printing, new tests are done at elevated pressure. These represent the more desired conditions in the gas stream, namely before the expander. Here it will be put as a deN₂O unit operation in sequence with the deNO_x installation. Preliminary results on deNO_x warrant the expectation that ECN's modified Fe/zeolite possibly in combination with other catalysts can remove NO_x as good as more traditional deNO_x units. Thus in the future it may even replace deNO_x.

A specific of applications is on vehicles equipped with a three-way catalysts. In large parts of the world these catalysts are mandatory for gasoline powered vehicles to remove CO, NO and a slip of hydrocarbons. However, when the catalysts age they generate more and more N₂O. ECN's modified Fe/zeolite catalyst may be just the solution. Car exhausts regularly contain enough unburnt hydrocarbons to make addition of a reducing agent superfluous. The simplest solution may be just to add a second honeycomb catalyst coated with modified Fe/zeolite just after the 3-way catalyst – no extras needed.

A third kind of applications is found in the clean-up of flue gases from various combustion facilities. The resistance of the catalyst against sulphur containing gases makes the catalyst suitable for this type of applications, including coal-fired power plants, waste incineration, combustion of sewage sludge, gas engines, diesel exhausts, etc. Basically, all exhausts that contain N₂O, NO_x can be tackled.

5. CONCLUSIONS

ECN has developed a Fe/zeolite catalyst for Selective Catalytic Reduction (SCR) of N_2O and NO using hydrocarbons as a reducing agent with the following characteristics:

- The catalyst is proven stable and active in N_2O removal.
- The catalyst is resistant against aggressive constituents in exhaust gases: O_2 , H_2O , CO_2 , NO_x and most importantly SO_2 .
- The catalyst does not emit CO and prevents slip of unburnt hydrocarbons.
- The catalyst has a large potential for NO reduction and for integrated N_2O + NO reduction.
- The catalyst may or may not need addition of hydrocarbon. When the gas already contains hydrocarbons, e.g., from incomplete combustion in the preceding operation, they might be present in sufficient quantities to perform SCR without extra addition.
- The catalyst can be used for reduction of N_2O and NO_x emissions from numerous sources, including nitric acid plants, caprolactam plants, adipic acid plants, car exhausts, power plants, incineration of municipal waste and sewage sludge.
- Using ECN's catalyst, the potential removal of N_2O emissions from nitric acid manufacture in the Netherlands is 8.5 Mton CO_2 equivalent.

Figure 1 Activity tests of Fe/zeolite. The most complex gas is composed of 500 ppm N_2O (or 250 ppm N_2O + 250 ppm NO), 1000 ppm C_3H_8 , 6% O_2 , 2% H_2O , 5% CO_2 , balance N_2 . Other mixtures were made by leaving certain components out

Figure 2 Comparison between Fe/zeolite of the first generation and Modified Fe/zeolite Gas is composed of 500 ppm N_2O , 1000 ppm C_3H_8 , 6% O_2 , 2% H_2O , 5% CO_2 , balance N_2